NIKITINA, Yu.P.: VOL'PIN, G.I.

Kubarla harizon of Paleocene sediments in the Yergeni Hills.

Sal-Manych interfluve, and lower Don. Mauch.dokl.vys.shkoly;geol.-geog.nauki no.1:89-93 '59. (MIRA 12:6)

1. Novocherkasskiy politekhnicheskiy institut.
(Yergeni Hills--Paleontology)
(Don Valley--Paleontology)

5.3400

77373 50V/79-30-1-34/78

AUTHORS:

Vol'pin, M. E., Akhrem, I. S., Kurpanov, D. H.

TITLE:

The Additions of Tropylium Salts to Vinyl Ethers

PERIODICAL:

Zhurnal obshehey khimit, 1960, Vol. 30, Nr. 1, pp. 159-

163 (USSR)

ABSTRACT:

Vinyl ethers vigorously react with tropylium salts.

$$X = 8r \cdot ClO_4$$
,  $A = C_2H_3 \cdot I_5 \cdot I_7 - C_3H_3 \cdot OCOCH_3$ 

Card 1/5

Tropylium salts react with vinyl ethyl-, vinyl isopropyl-, and vinyl n-butyl ethers in aqueous or in aqueous-alcohol, and only one product, cycloheptatrienylacetaldehyde, is formed. Tropylium bromide reacts similarly with  $\beta$ ,  $\beta$ -dimethylvinyl ethyl ether.

The Additions of Tropylium Salts to Vinyl Ethers

$$\begin{array}{c} (\overbrace{+}) \\ \text{Br} + \frac{\text{CH}_3}{\text{CH}_3} \\ \overbrace{\text{C}} = \text{CH} \\ \underbrace{\text{C}} \\ \text{C} \\ \text{C}_{\text{H}_3} \\ \text{H}_3 \\ \text{C} \\ \text{H}_4 \\ \text{C}_{\text{H}_3} \\ \text{OH} + \text{HBr} \\ \end{array}$$

Tropylium bromide with vinyl ethyl ether in anhydrous nitromethane forms a brominated product which could not be isolated, and is probably an  $\alpha$ -bromoether.

$$C_7\Pi_7^*Br^- + C\Pi_2 = C\Pi OC_2\Pi_5 \longrightarrow C_7\Pi_7C\Pi_2C\Pi < \frac{Br}{OC_2\Pi_5}$$

Card 2/5

Acetal and acid are formed by the above reaction in anhydrous alcohol. The acid formed complicates the isolation of the acetal.

The Additions of Tropylium Salts to Vinyl Ethers

77373 SOV/79-30-1-34/78

 $C_7H_7^+Br^- + CH_2 = CHOC_2H_5 + C_2H_5OH \longrightarrow C_7H_7CH_2CH(OC_2H_5)_2 + HBr.$ 

An attempt was made to prepare acetals by the reaction of vinyl ethers with ditropyl ether, but this reaction does not take place. The addition of tropylium salts (or an acid) (even in catalytic amounts) initiates a vigorous reaction. Ditropyl ether and vinyl ethyl ether in anhydrous alcohol form diethylacetal of cycloheptatrienylacetaldehyde, in good yield. The same reaction with vinyl butyl ether in anhydrous n-butyl alcohol yields di(n-butyl)acetal of cycloheptatrienylacetaldehyde. Probably an ionic chain reaction takes place in all cases, in which the tropylium cation serves as a carrier.

 $C_7H_7^+ + CH_2 = CHOR + ROH \rightarrow C_7H_7CH_2CH(OR)_2^+ + H^+$  $\frac{1}{2}(C_7H_7)_2O + H^+ \rightarrow C_7H_7^+ + \frac{1}{2}H_2O$ 

Card 3/5

The Additions of Tropylium Salts to Vinyl Ethers

77373 SOV/79-30-1-34/78

It can be assumed that the formation of a carbonium ion of type (I) is an intermediate stage of reaction, and that the above ion in nonhydroxylic solvents is converted into bromother (II); in alcohol, into acetal (III); and in water, into aldehyde (IV).

Card 4/5

Cycloheptatrienylacetaldehyde was obtained in 58% yield, bp 62°/2 mm, np  $^{20}$  1.5340,  $d_{\rm H}^{20}$  1.0204; cycloheptatrienyliso-butyric aldehyde, in 8.6% yield, bp 76-80°/3 mm,

The Additions of Tropylium Salts to Vinyl Ethers

77373 SOV/79-30-1-34/78

 $n_{\rm D}^{20}$  1.5201; wiethyl acetal of cycloheptatrienylacetaldehyde, in 72% bp  $102^{\rm o}/5$  mm,  $n_{\rm D}^{20}$  1.4876; dibutyl acetal of cycloheptatrienylacetaldehyde, in 75%, bp 130°/3 mm,  $n_{\rm D}^{20}$  1.4806,  $d_{\rm d}^{20}$  0.8188; diiso-propyl acetal of cycloheptatrienylacetaldehyde, in 75.6%, bp 96-100°/3 mm,  $n_{\rm D}^{20}$  1.4856. There are 4 references, 3 Soviet, 1 U.S. The U.S. reference is: W. E. Doering, L. H. Knox, J. Am. Chem. Soc., 76, 3203 (1954); 79, 352 (1957).

SUBMITTED:

January 5, 1959

Card 5/5

EWP(j)/EPF(c)/EWT(m)/BDS ACCESSION NR: AP3005440 AUTHORS: Vol'pin, M. Ye.; Dubovitskiy, V. A.; Nogina, O. V.; Kursanov, D. N. (Corr: Member AN SSSR) TITLE: Combining titanocene (dicyclopentadienyl titanium) SOURCE: AN SSSR. Doklady\*, v. 151, no. 5, 1963, 1100-1103 TOPIC TAGS: dicyclopentadienyl titanium ditolane, titanocene, dicyclopentadienyl titanium, tolane, diphenylacetylene, 1,2,3,4tetraphenylbutadiene, titanoceneditolane ABSTRACT: Because of its carbenoid character, dicyclopentadienyl titanium was selected for reaction with diphenylacetylene (tolane) in a 1:2 ratio to form the stable titanoceneditolane. The latter cleaved upon brominating to form titanocene dibromide and the dibromide of a Ti-free hydrocarbon. Heating, or treatment with aqueous or non-aqueous KOH, gave 1,2,3,4-tetraphenylbutadiene. Orig. art. has: 10 formulas. ASSOCIATION: Institute of organometallic compounds, Academy of sciences, SSSR Card 1/11

YOL PIN, M.Ye.; AKHREM, I.S.; TERENT YEVA, Ye.A.; KURSANOV, D.N.

Mechanism of tropylation reaction. Izv.AN SSSR.Otd.khim.nauk no.5:802-808 My '63. (MIRA 16:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR. (Tropylium compounds)

EWP(j)/EPF(c)/EWP(q)/EWT(m)/BDS Pc-4/Pr-4 L 17097-63 3/062/63/000/004/015/022 WW/JD Leytes, L. A., Dulova, V. G., and Vol'pin, M. Ye. AUTHOR: Three-membered heteroaromatic compounds. Report 5. Vibrational TITLE: spectra and the structure of germanium heterocyclics Investiya.: Otdeleniye khimicheskikh nauk, Akademiya nauk SSSR. PERIODICAL: no. 4, 1963, 731-737 The vibrational spectra of the three-membered germanium heterocyclics were studied to establish the structure of these compounds. The IFspectra of 1,1-disubstituted germirenes, 1,1-disubstituted 2,3-diphenylgermirenes and 1,1-dimethy1-2,3-diphenylsilirene were obtained in the range 400-3200 cm-1 on the UR-104spectrograph. The graphs are presented in one figure and the frequency and field intensities in one table. The combination scattering spectrum was taken for only one compound on the ISP-51 apparatus. The UVspectrum was taken for this compound also on the SP-41 double vacuum monochromatoscope. "The authors thank V.A. Petukhov for taking the UV-spectrum."

Card 1/2

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2" L 17097-63

S/062/63/000/004/015/022

Three-membered heteroaromatic.

There are 2 figures and 1 table.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR i Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organo-Elemental Compounds of the Academy of Sciences USSR and the Institute of Organic Chemistry, Academy

of Sciences USSR)

SUBMITTED: June 9, 1962

Card 2/2

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"

L 17065-63 EWP(j)/EPF(c)/EWP(q)/EWT(m)/ S/062/63/000/004/014/022

BDS AFFTC/ASD Pc-4/Pr-4 RM/WW/JD

AUTHOR: Vol.pin. M. Ye. Dulove V.G. and Kunseners D.W.

AUTHOR: Vol'pin, M. Ye., Dulova, V.G., and Kursanov, D.H.

TITLE: Three-membered heteroaromatic compounds. Report 4. Interaction between germanium di-iodide and acetylene, and the synthesis of a three-membered heterocyclic compound and a germanium-containing polymer.

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 4, 1963, 727-731

TEXT: The purpose of the study was to continue the research on formation of stable three-membered heterocyclic compound formed during the addition of germanium di-iodide on the triple carbon-carbon bend of diphenylacetylene and to obtain germanium heterocyclics with a simpler structure not containing the phenyl proups. GeI2 is added to acetylene at 130-140°, the reaction proceeding analogously to the addition to diphenylacetylene and resulting in the formation of the three-membered heterocyclic l.l-diiodogermirene (2,2-diiodo-

Card 1/3

L 17065-63

5/062/63/000/004/014/022

Three-membered heteroaromatic ....

9

2-germanium cyclopropene). During the reaction of of GeI<sub>2</sub> with acetylene, considerable quantities of polymeric products are obtained in addition to the three-membered cyclic. Infra-red and nuclear magnetic resonance spectra indicated the obtained polymer had the following structure:

$$- \begin{bmatrix} R & R & R \\ -CH = CH - Ge - CH = CH - Ge - \\ R & R \end{bmatrix}_{n}$$

where R = I, CH<sub>3</sub>, or C<sub>6</sub>H<sub>5</sub>. In structure these polymers are close to the so-called organic semiconductors and can represent great interest from the viewpoint of the character of the interaction of the pi-electrons in the polymer chain, since the interaction of pi-electrons of double bonds with d-orbits of germanium can contribute to partial delocalization of pi-electrons

Card 2/3

#### CIA-RDP86-00513R001860720014-2 "APPROVED FOR RELEASE: 08/09/2001

L 17065-63

\$/062/63/000/004/014/022

Three-membered heteroaromatic ...

in the polymer chain. There are 2 figures. The most important English-language reference reads as follows: K. B. Wiberg, B. J. Nist, J. Amer. Chem. Soc., 83,1226 (1961).

ASSOCIATION: Institut elementoorganicheskikh soyodineniy Akademii nauk SSSR (Institute of Organo-Elemental Compounds, Academy of Sciences

USSR)

SUEMITTED: June 9, 1962

Card 3/3

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"

## VOLPIN, M.

What did the audit show. Fin. SSSR 37 no.8:64-68 4g '63.

(MIRA 16:9)

1. Clavnyy kontroler-revizor kontrol'no-revizionnogo upravleniya
Ministerstwa finansov RSFSR.

(Ivanovo Province-Auditing and inspection)

# VOL'PIN, M.

Prisoner of local tendencies. Fin. SSSR 22 no.9:66-71 5 61. (MIRA 14:9)

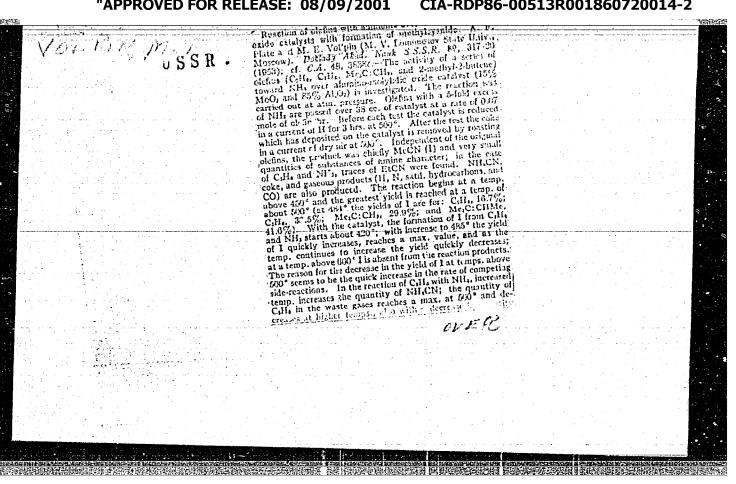
1. Glavnyy kontroler-revizor Kontrol'no-revizionnogo upravleniya Ministerstva finansov RSFSR.

(Banks and banking)
(Construction industry--Auditing and inspection)

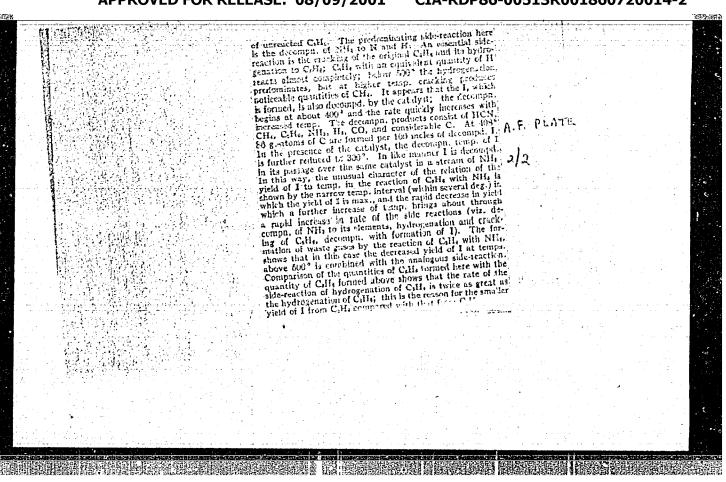
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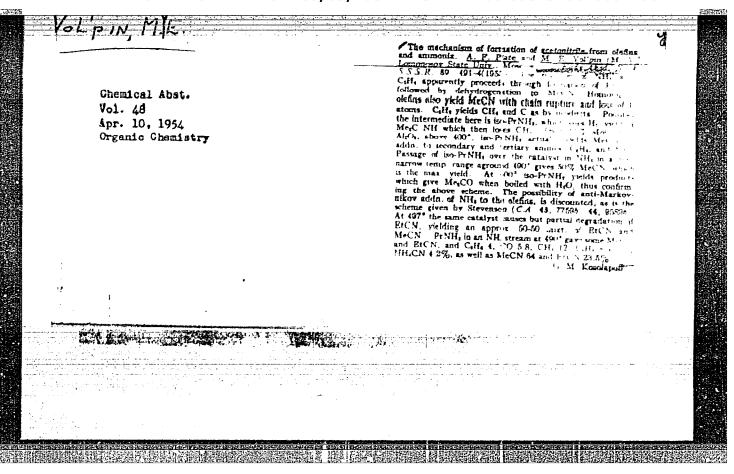
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VOL'PIN, M. Ye. and PLATE, A. F.

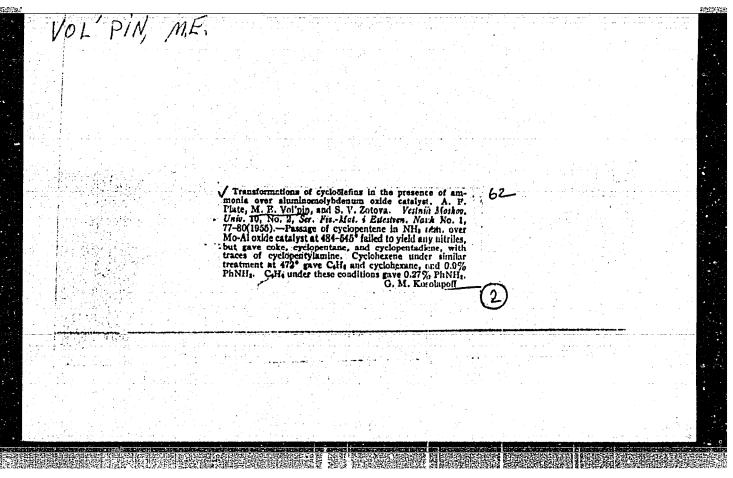
"Preparation of Acetonitrile by the Reaction Between Olefines and Ammonia in the Presence of Oxide Catalysts".

In the Presence of Oxide Catalysts In the Pr

Acetonitrile can be prepared by the reaction of NH3 with certain olefins in the presence of aluminum-molybdenum oxide catalysts. The activity of this catalyst can be increased by preliminary reduction of the Mo catalyst. The catalyst is further reduced furing the course of the reaction, with the maximum yield of acetonitrile being achieved after 3 hours of work. Small additions of oxygen or air selectively poison the catalyst and retard coking, thus increasing the yield of acetonitrile by 1.5 times. Pure Al<sub>2</sub>O<sub>3</sub> has no catalytic activity in the olefin-ammonia reaction. (RZhKhim, No 4, 1955)

SO: Sum No 884, 9 Apr 1956

#### 



USSR/Chemistry organic

FD-1604

Card 1/1 : Pub. 129-9/25

Author

: Plate, A. F.; Vol'pin, M. Ye.; Zotova, S. V.

Title

Transformation of cycloolefins in the presence of ammonia over alu-

minum and molybdenum oxide catalyst

Periodical

: Vest. Mosk. un., Ser. fizikomat. 1 yest. nauk, Vol 10, 77-80, Feb 1955

Abstract

: Cyclic olefins (cyclopentene and cyclohexene) behave in a manner different from that of the straight chain olefins when treated with ammonia in the presence of molybdenum oxide on aluminum oxide catalyst. There is no detectable formation of acetonitrile or of any higher nitriles. Hydrogen disproportionation and dehydrogenation predominate. Under the experimental conditions, cyclohexene and benzene react with a ammonia to form a small amount of aniline. Equation, two tables; nine

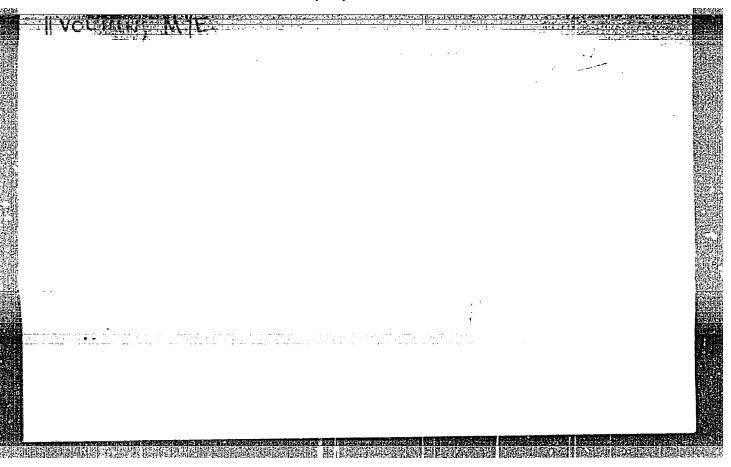
references (eitht USSR

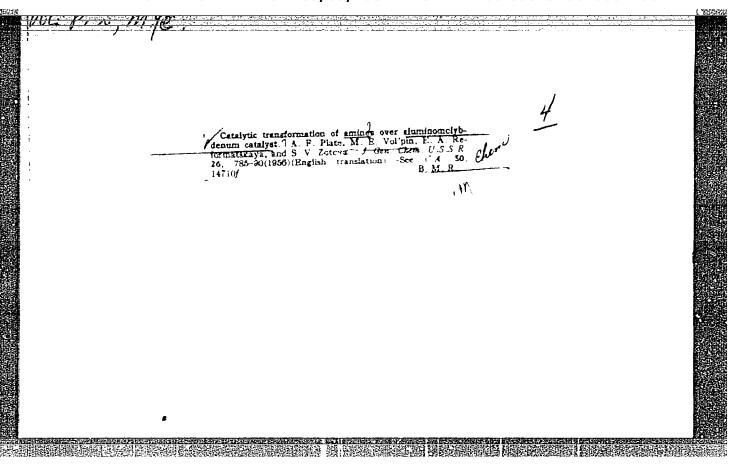
Institution : Chair of Petroleum Chemistry

Submitted

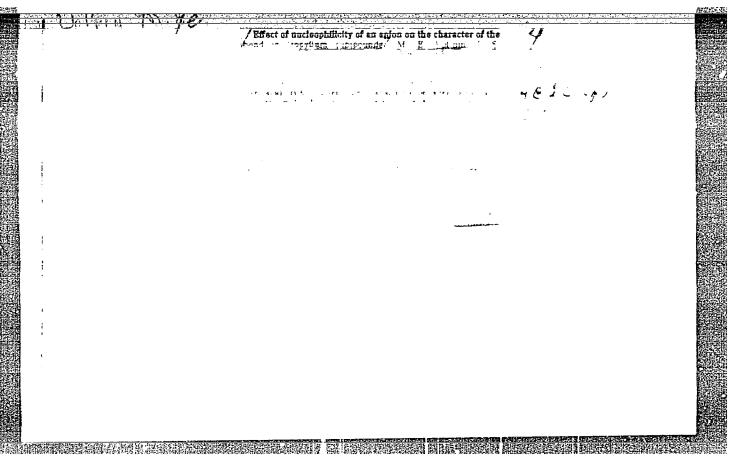
: June 23, 1954

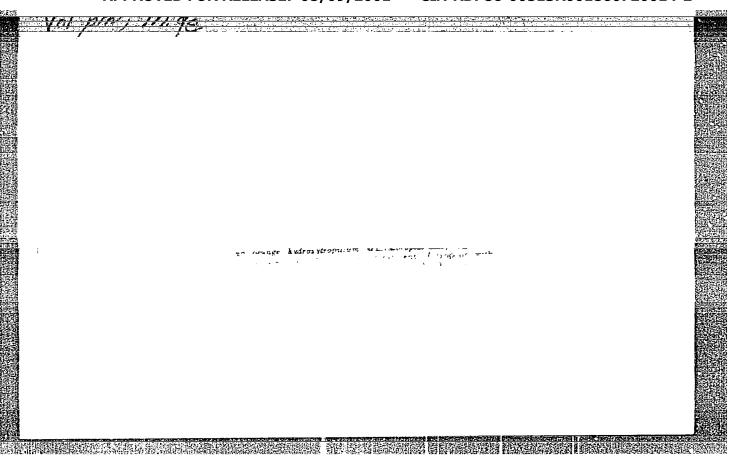
APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"





## 





VOL'PIN, M.YE. 62-11-12/29 Kursanov, D.N., Vol'pin, M. Ye., Akhrem, I. S., Kachkurova, I. Ta. AUTHORS: Curtius' (Kurtsius) Rearrangement in the Series of Isomeric TITLE: Cycloheptatrienecarbonic and Norcaradienecarbonic Acids (Peregruppirovka Kurtsiusa v ryadu izomernykh tsiklogeptatriyenkarbonovykh i norkaradiyenkarbonovoy kislot). Izvestiya AN SSSR, Otdelenie Khimicheskikh-Nauk, 1957, PERIODICAL: Nr 11, pp. 1371-1378 (USSR) Here Curtius' rearrangement in the series of isomeric  $\alpha$ -cycloheptatrienecarbonic-(I), (R = COOH),  $\beta$ -cyclohepta-ABSTRACT: trienecarbonic-(II) (R = COOH), y-cycloheptatrienecarbonic -(III) (R = COOH) acids are systematically investigated. It is shown that the rearrangement takes place under the conditions here existing without an isomerization of the migrating hydrocarbon radical. For the first time here 1,3,5-, 1,3,6- and 2,4,6- cycloheptatrienylisocyanate, norcaradienylisocyanate, 1,3,5,-1,3,6, and 2,4,6-cycloheptatrienylurea, norcaradienylurea, N-phenyl-N'-1,3,5-, 1,3,6- and 2,4,6-cycloheptatrienylurea Card 1/2

**AUTHORS:** 

Vol'pin, K.Ye., Akhrem, I.S., Kursanov, D.N.

62-12-20/20

TITLE:

Letters to the Editor (Pis'ma redaktoru)

New Reactions of Tropyl Salts (Novyye reaktsii soley tropiliya).

PERIODICAL:

Izvestiya AN SSBR Otdeleniyo Khimicheskikh Nauk, 1957, Nr 12,

pp. 1501-1502 (USSR)

ABSTRACT:

It was shown that the salts of cycloheptatrienyl very easily alkylate the compounds with mobile hydrogen. Tropyl salts react with the same ease with various aliphatic aldehydes. Aliphatic and arcmatic ketones when heated also enter into reaction with the salts of tropyl. The latter easily alkylates numerous aromatic compounds. Propyl differs from the other simple esters by the fact that it alkylates the esters of 3-keto acids, 3 -diketones, and 3 -dicarbonic acids easily in the case of soft conditions. Thus, cycloheptatrienylacetine acid ester is formed with aceto acid ester. The tropyl salts easily attach themselves to the compounds with activated short bonds (like vinyl esters, cyclopentadien, phenyl acetylene, and others). The reactions investigated offer new possibilities for the synthesis of the derivatives of cycloheptatrien and

Card 1/2

tropyl. There are 4 references, 3 of which are Slavic.

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2" Letters to the Editor. New Reactions of Tropyl Salts

62-12-20/20

ASSOCIATION:

Institute for Elemental-organic Compounds AS USSR (Institut

elementoorganicheskikh soyedineniy Akademii nauk SSSR).

SUBMITTED:

October 9, 1957

AVAILABLE:

Library of Congress

Card 2/2

1. Tropyl salts-Reactions

USCOMM-DC-54782

VOL'PIN. M.Ye.; ZHDANOV, S.I.; KURSANOV, D.N.

New tropilium salts. Tropilium ion polarography. Dokl. AN SSSR 112 no.2:264-266 Ja 157. (MIRA 10:4)

1. Chlen-korrespondent AN SSSR (for Kursanov). 2. Institut elementoorganicheskikh soyedineniy i Institut fizicheskoy khimii Akademii nauk SSSR.

(Cycloheptatrienyl)

VOLPIN, M.Ye. AUTHOR KURSANOV D.N., Corresponding Member of the Academy

XXXXXXXXXXX 20-2-27/67

TITLE

A New Method For Production of Tropilium And Metatropilium

Compounds.

(Novyy put'polucheniya soyedineneiy tropiliya i metatropiliya

-Russian)

PERIODICAL

Deklady Akademii Nauk SSSR, 1957, Vol 113, Nr 2, pp 339-342 (U.S.S.R.) Reviewed 7/1957

Received 6/1957

ABSTRACT

At present two fundamentally different ways of producing the 7term aromatic tropilium-system are knwen: 1.methed: tropiliumdibromide (including small quantities of salts of the carboxyltrepilium) is obtained by separating HBr dibromal cycloheptadicne. 2.method: This method is based on the slight isomerization of a norkadiene-system into a tropilium-system. However, it would doubtlessly be interesting to investigate the possibility of a direct transition from the cycloheptatriene-system (IV) (tropilidene) with 3 double bonds to the aromatic tropilium-system. A conjugation of all of the six double bond- $\pi$ -electrons must be possible which is realized in consequence of the separation in any way of a hydrogen atom together with an electron pair from the CH2-group of the cycloheptatriene and then at the same time the transition of the 7th carbon atom from the sp3-hybridization condition into the sp2- hybridization condition must be possible, which would lead to the formation of the aromatic tropilium-system. Here a nonbenzeid

Card 1/3

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"

A New Method For Production of Tropilium And Metatropilium Compounds.

20-2-27/67

aromatic system ox-electrons would develop. When studying this direct transformation from cyclopentadienes into tropilium salts the authors investigated the influence of a number of electrophile reagents, strong acids, oxidation agents, haloid derivatives etc. on tropilium salts. On the occasion of an influence of concentrated sulphuric acid on cycloheptatrienes an exethermic reaction accompanied by formation of resin develops. However, a tropilidene exydation together with formation of censiderable quantities of tropilium salts (18%) takes place. Acids without any exidizing properites (concentrated phospheric acid, hydrechleric acid) de not lead to a fermation of trepilium. Cencentrated nitiric acid reacts very turbulently with cycloheptatriene, and small quantities of trepilium develop. Other exidation agents in acid media effect a slighter er strenger transfermatien ef cycleheptatriene into tropilium (CrO3 - 14%, SeO2-7% yield of tropilium salt). Phosphorus pentachleride very slightly reacts with cycleheptatriene at normal reem temperature. Trepilium chleride develops and PCl<sub>5</sub> is reduced to PCl<sub>3</sub>. This reaction can serve as a good preparátien methed fer préducing trepilium salts. It is better te prepare trepilium as a more continuous, net very hygroscepic, net easily soluble perchlorate, chloroplatinate or iodide. The same

Card 2/3

A New Method For Production of Tropilium And Metatropilium Compounds. 20-2-27/67

method is applicable for the preparation of methyltropilium salts (II,R=CH<sub>2</sub>) by the influence of phosphorus pentachleride on methylcycloheptatriene. On the other hand neither phosphorus trichleride nor phosphorus tribromide is able to effect this transformation. Similar to the reaction with phosphorus pentachloride the other proceeds with suluryl chloride. 25% tropilium salt develop with considerable resinification. Thionyl chloride does not react with cycloheptatriene. In the experimental part experimental conditions are described in detail. (With 6 citations from publications).

ASSOCIATION PRESENTED BY

Institute for element-organic Compounds of the Academy of Science of the U.S.S.R.

SUBMITTED AVAILABLE

Card 3/3

16.10.1956

Library of Cengress

KURSANOV, D.N.; VOL'PIN, M.Ye., kand. khim. nauk; PARNES, Z.N., kand. khim.

New aromatic systems, Report No.1: Tropylium cation and cyclopentadienyl anion as nonbensene aromatic systems. Khim, nauka i prom. 3 no.2:159-173 \*58. (MIRA 11:6)

1. Chlen-korrespondent AN SSSR (for Kursanov).
(Organic compounds)
(Cycloheptatrienylium compounds)
(Cyclopentadienyl)

VOL'PIN, MYE

79-2-10/55

AUTHORS:

Vol'pin, M. Ye., Akhrea, I. S., Kursanov, D. H.

TITLE:

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds (Vliymniye nuklcofil nosti aniona na kharakter svyazi v soyedineniyekh tropiliya)

PERIODICAL:

Zhurnal Obshchey Khimii, 1950, Vol. 28, Nr 2, pp. 330 - 333 (USSR)

ABSTRACT:

A number of salts of the aromatic 7-member cation of cycloneptatrienyl (tropilium) was recently produced (references 1 to 3). They are all salts of sufficiently strong acids (X = Cl, Br, J, ClO, PtCl<sub>6</sub>, B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, NCO). On the other hand the tropiliumoxide, adthoxytropilium, tropilium cyanide, tropiliumthioether (references 1 and 2), where the X is an anion of sufficiently weak acids, are covalent compounds of type (II). Here and further the authors leave open the question whether the covalent tropilium derivatives possess a cycloheptatriene- or norcadiene structure (cf. reference 4). The authors made it their tak to determine the boundary where the ionic compound C<sub>7</sub>H<sub>7</sub>+X transforms into the covalent compound C<sub>7</sub>H<sub>7</sub>-X. For this purpose they synthesized tropilium derivatives of acetic and benzoic acids (K<sub>a</sub> = 1.75.10-5 and 6.3.10-5). As well the tropilium acetate as the tropilium benzoate (more exactly the cycloheptatrienylacetate and benzoate) proved to be typically covalent

Card 1/4

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds

compounds - liquids - which can be solved in nonpolar solvents. Thus the transition from the donic salts of tropilium to the covalent derivatives lies in the interval K of the corresponding acids. These results agree with the data by Dering (reference 1) that the tropilium ion behaves in water like the acid K =1.8.10 and reacts according to the educe

The results obtained point to the assumption that the acids with  $K_a > 1.2.10^{-4}$  will yield ionic salts with tropilium: the acids  $K_a > 1.2.10^{-4}$  will yield ionic salts with tropilium: the acids  $K_a > 6.8 - 1.75.10^{-2}$  must yield covalent compounds with tropilium. This result is confirmed by the results of the interaction of tropilium bromide or tropilium perchlorate and cyclopentadienilitium. The formation of the covalent compound is explained by the work acid properties of cyclopentadiene and consequently by the considerable nucleophilia of the anion  $C_cH_c$ . The tropilium acetate and benzoic enhydrides. This method of ether production may have quite a general importance. The attempts to produce tropilium acetate by means of an exchange reaction of tropilium perchlorate and potassium

Card 2/4

CONTROL OF THE CONTRO

The Influence Exerted by the Nucleophilia of the Anion Upon the Mature of Linkage in Tropilium Compounds

acetate in water and in alcohol were unsuccessful. Heither was it possible to produce tropilium benzoate by the exchange of potassium benzoate and tropilium perchlorate in water, nor by an exchange reaction of silver benzoate and tropilium bromine in alcohol or nitrone thane. This indicates the instability of the cycloheptatrienyl ether and the inclination to hydrolysis. The covalent coupound C7H7-X in tropilium cyanide and tropiliumcyclopentacienyl proved to be considerably stabler. It is interesting that in the acid process of the hydrolysis of tropilium cyanide a partial isomerization supposedly takes place and that phenylacetic acid is formed. Conclusions: 1) Tropilium acetate, -benzoate and cyclopentadienylcycloheptatriene which proved to be covalent compounds were produced. 2) It was shown that the nature of linkage of the cyclo-hertatrienyl residue with the anion depends on the nucleophilia of the anion. The transition from ionic to covalent tropilium de-rivatives lies in the range of K from 1.2 10-4 to 5.3 - 1.75.10-5. 3) It was shown that in the case of an acid hydrolysis of tropilium cyanide a regrouping with the formation of phenylacetic acid takes place. There are 6 references, 2 of which are Slavic.

Card 3/4

79-2-10/64

The Influence Exerted by the Nucleophilia of the Anion Upon the Mature of Linkage in Tropilium Compounds

ASSOCIATION:

Institute for Elemental-organic Compounds AS USSR

(Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

SUBLITTED:

April 15, 1957

AVAILABLE:

Library of Congress

Card 4/4

# "APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2

SOV/ 20-120-3-26/67

AUTHORS:

Kursanov, D. N., Corresponding Member, Academy of Sciences,

USSR, Vol'pin, M. Ye., Akhrem, I. S.

TITLE:

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β-Chloroacetaldehyde (Reaktsiya soley tropiliya s vinilovymi

efirami i β-khlormerkuratsetal'degidom)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 3, pp. 531-534

(USSR)

ABSTRACT:

A characteristic property of the stable aromatic cation of cycloheptatrienylium (tropylium) is represented by its capability to react with nucleophilic reagents. (Ref 1). It was to be expected that the electrophilic property of the tropylium cation is sufficient also for a reaction with more weakly nucleophilic reagents, as vinyl ethers. This actually was the case, as the tropylium salts react with simple vinyl ethers in aqueous or alcohol solutions even in the cold under a self-heating. This high reactivity is a result of the influence of the electron-donor ether group. Compounds with isolated or conjugated double bindings, however, without

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**SOV2**0-120-5-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercu.y  $\beta$ -Chloro-acetaldehyde

activating substances (as, for example, methylcyclohexene, cycloheptatriene and others), or with electron accepting substituents (cinnamic acid, acrylic acid, acrylonitrile, chloroallyl and others) do not react with tropylium salts under identical conditions. In all cases the same product results independent of the nature of the anion of the initial salt of tropylium (whether bromile or perchlorate) and independent of the character of the alkyl in the vinylalkyl ethers: cycloheptatrienyl acetaldehyde. This reaction is analogous to that of the addition of mercury salts to vinyl ethers (Ref 2). Therefore it could be assumed that the mechanism of interaction of the tropylium salts with vinyl ethers includes an attack upon the double binding of the vinyl ether by the ion  $C_{\eta}H_{\eta}$  . At the same time, or subsequently, an action of one molecule of the solvent (water or alcohol) takes place. An acetal or a semi-acetal is probably the intermediate prodnot of the reaction. The reaction velocity with the tropylium salts is markedly reduced at the transition from the simple vinyl ether to the vinyl acetate. This apparently is connected with a partial withdrawal of electrons by the C=O group.

Card 2/4

soy20-120-3-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β-Chloro-acetaldehyde

Cycloheptatriene acetaldehyde was also obtained by a counter synthesis, that is to say by a reaction of the tropylium salts (bromide or perchlorate) with mercury  $\beta$ -chloroacetaldehyde. Because of an exchange of an Hg-atom with a tropylium radical an aldehyde was produced, which was identical with that produced from vinyl ethers. This is the first case to be investigated of an interaction of organomercury compounds with tropylium salts. The reaction of the tropylium salts with mercury  $\beta$ -chloroacetaldehyde proceeds according to the type of C-alkylation. The haloid acyls O-acylate mercury  $\beta$ -chloroacetaldehyde. There are 4 references, 3 of which are Soviet.

ASSOCIATION:

Institut elementoorganicheskikh soyedineniy Akademii nauk

SSSR

(Institute of Elemental-organic Compounds AS USSR)

Card 3/4

# "APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2

SOV/20-120-3-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β-Chkroacetaldehyde

SUBMITTED:

January 14, 1958

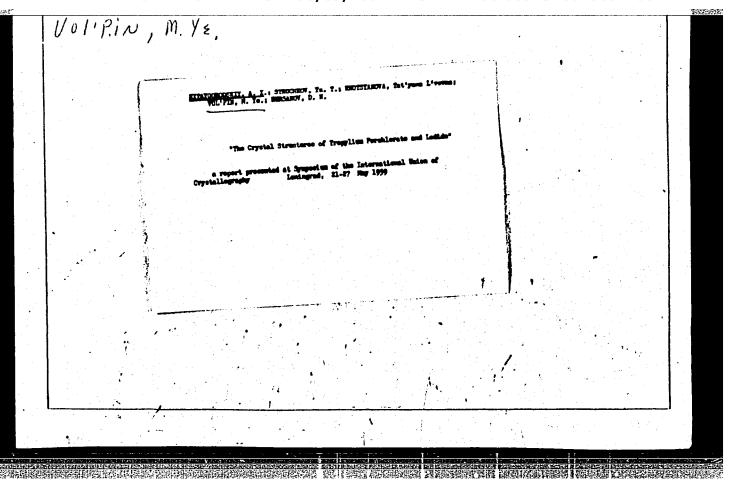
1. Tropylium salts--Chemical reactions 2. Vinyl ethers--Chemical reactions 3. Mercury compounds (organic)--Chemical reactions

Card 4/4

VOL'PIN, M. Ye. Doc Chem Sci -- (diss) "Study of nonbenzoid aromatic systems of tropyl and cyclopropenyl." Mos, 1959. 20 pp (Acad Sci USSR. Inst of Elementoorganic Compounds), 150 copies (KL, 52-59, 116)

-13-

# "APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2



APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"

#### "APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2

5(4)

AUTHORS: Vol'pin, M. Ye., Koreshkov, Yu. D., SOV/62-59-3-34/37

Kursanov, D. N.

TITLE:

Diphenyl Cyclopropenone - Three-membered Analogue of Tropone

(Difeniltsiklopropenon - trekhchlennyy analog tropona)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1959, Nr 3, p 560 (USSR)

ABSTRACT:

In this letter to the editor the authors write: We obtained

diphenyl cyclopropenone (I) (melting point 121°,  $\lambda_{\text{max}}$  339 and 291 m $_{\mu}$ ; computed for  $c_{15}H_{10}O$ : C 87.36 %, H 4.88 %,

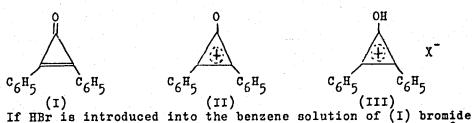
M = 206). This is the first unsaturated 3-membered ketone to be described. In spite of the considerable angular tension in the cycle (I) is a stable substance. It forms 2,4-dinitro phenyl-hydrazone (melting point  $248-249^{\circ}$ ). In the hydration in alcohol over platinum black it absorbs 2 mol  $H_2$ . Two intense absorption bands within the range of 1,600 and 1,850 cm<sup>-1</sup> may

be observed in the infrared spectrum.

Card 1/3

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2" Diphenyl Cyclopropenone - Three-membered Analogue of Tropone

sov/62-59-3-34/37



forms (in form of a monohydrate, melting point 148.5-149.0°; per cents computed for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>Br: C 59.03, H 4.30, Br 26.19; % found: C 58.87, H 4.37, Br 25.89) from which the initial ketone may be regenerated by the action with weak bases. Similar salts form with HCl and HJ. The salt-forming properties of (I) as well as its anomalously high dipole moment 5.08 D (it was determined by Ya. K. Syrkin and A. N. Shidlovskaya) are due to the tendency of the cyclopropenone ring towards the formation of a stable aromatic system of cyclopropenyl (II). By the action of acids (I) is transformed into cation salts of diphenyl oxycyclopropenyl (III). Thus, cyclopropenone

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Diphenyl Cyclopropenone - Three-membered Analogue of Tropone

sov/62-59-3-34/37

derivatives are analogues of tropone which has the tendency to form the 7-membered aromatic system of tropyl. (I) was obtained by the action of dibromo carbene (from bromoform and tertiary potassium butylate) on diphenyl acetylene with subsequent hydrolysis. This reaction is the first case of an interaction between dihalogen carbenes and compounds containing a triple bond. The applicability of this reaction in the production of other cyclopropenones will be further investigated.

ASSOCIATION:

Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of

Sciences, USSR)

SUBMITTED:

January 9, 1959

Card 3/3

5(4) AUTHORS:

Vol'pin, M. Ye., Zhdanova, K. I., SOV/62-59-4-37/42

Kursanov, D. N., Setkina, V. N., Shatenshteyn, A. I.

TITLE:

On the Interaction of Tropilium Salts With Electrophilic Reagents (O vzaimodeystvii soley tropiliya s elektrofil'nymi

reagentami)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1959, Nr 4, pp 754-755 (USSR)

ABSTRACT:

This is a brief communication on the investigation of the deuterium exchange of tropilium salt in anhydrous D<sub>2</sub>SO<sub>4</sub>.

It was found that at room temperature the tropilium ion does not take part in the reaction of the deuterium exchange even in the course of 168 hours. Thereafter the deuterium exchange was investigated under aggravated conditions, in liquid DBr in the presence of AlBr<sub>3</sub>. It was found that tropilium bromide

does practically not exchange the deuterium even under aggravated conditions, with AlBr3 excess. (The exchange amounts to no more than 0.9 % in the course of 94 hours). The experiments

showed a strong restraint of the electrophilic attack in tropilium salts. In this respect tropilium turned out to

Card 1/2

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"

On the Interaction of Tropilium Salts With Electro- 50V/62-59-4-37/42 philic Reagents

be considerably more inactive than benzene and even unsaturated hydrocarbons. The cause of such a difficult course of the electrophilic substitution in the tropilium ion might be that all carbon atoms of the tropilium ring have a positive charge and the system has an electron deficit. This is in accordance with the general conception of the effect of the charge on the deuterium exchange (Ref 5). It can be expected that also other electrophilic reactions will be as little characteristic of the tropilium ion and as difficult as the deuterium exchange. There are 7 references, 4 of which are Soviet.

ASSOCIATION:

Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds of the Academy of Sciences, USSR). Fiziko-khimicheskiy institut im. Karpova (Physico-chemical Institute imeni Karpov)

SUBMITTED:

September 7, 1958

Card 2/2

sov/79-29-2-70/71

AUTHORS:

Belova, V. I., Vol'pin, M. Ye., Syrkin, Ya. K.

TITLE:

Letter to the Editor (Pis'mo v redaktsiyu)

The Magnetic Receptivity of Tropyl Salts (Magnitnaya vospriimchivost

soley tropiliya)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 693-694 (USSR)

ABSTRACT:

The compound C7H7 is known to be stable in the cyclic structure form of the positively charged C7H7 ion. It is of interest to determine the diamagnetic receptivity of this ion and to compare it with the receptivity of other cyclic molecules, e.g. benzene and cyclooctatetraene. For this purpose the following compounds were synthesized and their receptivity was determined: tropyl hexachloro platinate (C7H7)2PtCl6, tropyl perchlorate C7H7ClO4 and tropyl mercury tetraiodide (C7H7)2HgJ4. A report on the synthesis of the first two compounds had already been made earlier (Ref 2). Tropyl mercury tetraiodide was first synthesized as follows: aqueous HgCl2-solution and KJ were added to  $C_7H_7Br$  solved in water (2.34 g, 3.72 g, and 9.1 g,

Card 1/3

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"

SOV/79-29-2-70/71

Letter to the Editor. The Magnetic Receptivity of Tropyl Salts

respectively).  $(c_7H_7)_2HgJ_4$  was separated and filtered, washed with 10 % KJ solution of water and alcohol and finally recrystallized from nitromethane. The magnetic receptivity was determined according to Saxsmith (Saksmit) at room temperature and with certain strength values of the magnetic field (Table 1). Unlike other platinates, the receptivity values of tropyl chloro platinate differ from one another in various syntheses. The table shows therefore the highest determination of receptivity, which surely corresponds to the purest sample (from the magnetic point of view). The value of magnetic receptivity in the organic cations of tropyl C7H7+ was calculated from experimental data. The anion value of receptivity is given in the fourth column of the table. The receptivity value of ion Pt Cl was determined according to reference 3, that of the ion HgJ<sub>4</sub><sup>2-</sup> according to reference 4. The value of ion ClO<sub>4</sub><sup>-</sup> was obtained from table 3 (from the book by Selwood, P.W.) (Ref 5). The value of receptivity of ion C7H7+, from various tropyl compounds, is recorded in the last column of the table. Pascal's additive scheme concerning the receptivity values of the compounds, containing conjugate bonds

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501/79-29-2-70/71

Letter to the Editor. The Magnetic Receptivity of Tropyl Salts

(C6H6, C7H7+, C8H8) is judged negatively by the authors and their own explanations are given. There are 1 table and 6 references, 2 of

which are Soviet.

ASSOCIATION: Institut obshchey i neorganicheskoy khimii i Institut elemento-

organicheskikh soyedineniy Akademii nauk SSSR (Institute for General and Inorganic Chemistry and Institute for Elemental-organic Compounds

of the Academy of Sciences, USSR)

SUBMITTED: July 20, 1958

Card 3/3

507/79-29-9-10/76

5(3) AUTHORS: Vol'pin, M. Ye, Akhrem, I. S., Kursanov, D. N.

TITLE:

Reaction of Tropylium Salts With Aldehydes

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 9,

pp 2855 - 2857 (USSR)

ABSTRACT:

The present paper deals with the investigation of the reaction of tropylium salts with aldehydes, basing on the papers quoted by references 1,2. Owing to the mobility of  $\alpha$ -hydrogen atoms of aldehydes, hydrogen is readily replaced by deuterium or bromine in the latter (Ref 3). Various con-

densations are made possible thereby:

$$-c \longrightarrow c \longrightarrow c \longrightarrow c \longrightarrow h^+$$

The authors found the cation of tropylium to react likewise with aldehydes. Already at room temperature (but more rapidly and in better yields at higher temperatures) one of the  $\alpha$ hydrogen atoms of aldehyde is replaced by the cycloheptatrienyl residue:

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APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2" Reaction of Tropylium Salts With Aldehydes

507/79-29-9-10/76

This course is followed by the reaction of tropylium bromide with acetic, propionic, isobutyric acid aldehyde, which contain three, two of one α-hydrogen atom, respectively. Monosubstituted aldehydes (I),(II),(III) were obtained in all cases. Tropylium salts react likewise with isovaleraldehyde and other aldehydes, whereas benzaldehyde, which has no α-hydrogen atoms, does not enter reaction with the above salts even not with longer heating. The structure of cycloheptatrienyl acetic and α-cycloheptatrienyl isobutyric acid aldehyde was proven by the identity with aldehydes forming in the addition of tropylium salts on the corresponding vinyl ethers (Ref 4) (Scheme 3). The frequency, typical of the carbonyl group, in the infrared spectra of the aldehydes obtained shows that there is no conjugation of the C=O group with the C=C double bonds occurring in them. Thus, tropylium salts

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Reaction of Tropylium Salts With Aldehydes

507/79-29-9-10/76

were shown to react (under no rigorous conditions) with aldehydes containing  $\alpha$ -hydrogens, under the formation of a new C-C bond. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR(Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED: August 22, 1958

Card 3/3

907/20-126-4-25/62 5(3) Corresponding Member AS USSR Kursanov, D. N., Vol'pin, M. Ye.; AUTHORS:

The Effect of Hydrogen Peroxide on Tropilium Salts (Deystviye TITLE: perekisi vodoroda na soli tropiliya). A New Reaction Involving a Narrowing of a Seven-member Cycle (Novaya reaktsiya suzheniya

semichlennogo tsikla)

Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 4, pp 780-783 PERIODICAL:

(USSR)

Several examples are known of rearrangements of tropon and ABSTRACT: tropolon derivatives under the influence of cationic reagents (Ref 1). Benzene derivatives develop, containing the same number of carbon atoms as the original compound. Tropilium salts are subject to an analogous change. They are transformed into benzaldehyde under the influence of oxidizers (Refs 2, 3). The authors found out however, that the reciprocal action of tropilium salts and hydrogen peroxide involve a narrowing of the seven-member cycle, developing in another direction than described above. If equimolecular amounts of the two mentioned substances are mixed in a hydrous solution, a quick exothermal reaction develops. Its main products are:

benzene, CO, formic acid and hydrogen bromide (Table 1). Furthermore small amounts of benzaldehyde and phenol develop.

Card 1/3

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2" The Effect of Hydrogen Peroxide on Tropilium Salts. A New Reaction Involving a Narrowing of a Seven-member Cycle

Thus the process on the whole takes place in two directions (see scheme). The authors studied the kinetics of the first two reactions (where CO develops). This reaction taking place with great velocity, follows an equation of second order. A greater increase in the acidity of the medium slows it down, but slightly. The apparent activation energy between 20 and 50° is much lower than in typically organic reactions. The mentioned reaction can hardly be called a radical one. From the results achieved one may draw the conclusion that in the first bimolecular phases of the reaction, a reciprocal action of the tropilium ion and  ${\rm H_2O_2}$  takes place, and an inconstant hydrogen peroxide develops (I). It is the tropilium ion which takes part in this reaction, and not its dissociated salt. It is possible, however, that (I) either decomposes with an immediate development of reaction products or that it first changes into a cation (II). The latter first splits into benzene and  $\mathrm{HCO}^+$  cation. One could also believe that the reaction passes an intermediate state where tropon is produced. Tropon however, does not decompose into benzene and

Card 2/3

SOV/20-126-4-25/62

The Effect of Hydrogen Peroxide on Tropilium Salts. A New Reaction Involving a Narrowing of a Seven-member Cycle

CO. Neither is it possible that the reaction passes an intermediate state of benzaldehyde. Thus the reaction of the narrowing of the cycle studied here, differs from analogous reactions in so far, as it takes place under the synchronous splitting-up of two carbon linkages, at the same time developing a non-substituted benzene cycle. In this regard it is possible to compare it to the reactions of the 1,4-elimination of some bicyclic systems (Ref 5) (see scheme). There are 1 figure, 1 table, and 5 references, 2 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk

SSSR

(Institute of Elemental Organic Compounds of the Academy of

Sciences, USSR)

SUBMITTED: March 24, 1959

Card 3/3

5.3600

66171

SUY/20-128-5-24/67

AUTHORS:

Vol'pin, M. Ye., Dulova, V. G., Kursanov, D. N., Corresponding

Member, AS USSR

TITLE:

Formation of Tropilium in the Reaction of Monohalocurbenes

With Benzene

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 5,

pp 951 - 952 (USSR)

ABSTRACT:

The reaction of hydrogen peroxide with tropilium salts causes the elimination of one carbon atom and benzene formation as was proved by the authors some time ago (Ref 1). An inverse reaction, however, has so far not been known (extension of the benzene cycle with the formation of a tropilium cation). There exist only indirect data (Ref 2). The authors have proved that small quantities of tropilium bromide are formed in all cases if potassium tert-butylate acts on CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub> or

CH2J2 in a benzene medium and hydrogen bromide treatment follows.

This may be explained by intermediate formation of the monohalocarbenes CHX and their interaction with benzene (see Diagram). The concentration of the initial substances and the

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Formation of Tropilium in the Reaction of Monohalocarbenes With Benzene 507/20-128-5-24/67

duration of reaction are of no importance for the yield. The tropilium yield increases slightly with temperature. The reaction investigated by the authors is the first case of formation of nonsubstituted monohalocarbenes observed. The rate of alcoholysis of haloid methylenes increases following the  $S_N^2$  mechanism according to the order  $\text{CH}_2\text{Cl}_2$   $\text{CH}_2\text{Br}_2$   $\text{CH}_2\text{J}_2$  (Ref 4) whereas the yield of the tropilium salt increases in inverse order (in agreement with reference 5). There are 6 references, 2 of which are Soviet.

ASSOCIATION:

Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED:

June 29, 1959

Card 2/2

# "APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2

AUTHORS: Kitaygorodskiy, A. I Struchkov, Yu. T. Khod. T. L., Yol'pin, M. Ye., Kurkanov, D. N.  TITLE: Crystal Structure of Tropyllum Perchlorate on Following and 1960, Nr 1, pp 39-44 (USSR)  ABSTRACT: X-ray diffraction study of the structure of tropyllum perchlorate and iodide monocrystals was made, using the method of three-dimensional electron density of the following cell constants are given:  (C.H.  CO.    C.H.  CO.    C.H.     C.H.     (C.H.  CO.    (C.H.  CO.    (C.H.     (C.H.  CO.		
TITLE: Crystal Structure of Tropylium Perchlorate on toll  PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye knii in nauk, 1960, Nr 1, pp 39-44 (USSR)  ABSTRACT: X-ray diffraction study of the structure of transition perchlorate and iodide monocrystals was made, unit the method of three-dimensional electron density the following cell constants are given:  (C.H.)(CO.) (C.H.)(CO.) (C.H.)(I)  a=b(\hat{\lambda}\) 2.33\frac{1}{2}.04 2.01\frac{1}{2}.02 (\hat{\lambda}\) 8.54\frac{1}{2}.05 (\hat{\lambda}\) 8.54\frac{1}{2}.05 (\hat{\lambda}\) 4.14 (-1.8 (\hat{\lambda}\) 4.10 (\hat{\lambda}\) 4	j.3100	$rac{7300}{300}$
PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye kinimauk, 1960, Nr 1, pp 39-44 (USSR)  ABSTRACT: X-ray diffraction study of the structure of transit perchlorate and iodide monocrystals was made, unimate method of three-dimensional electron density the method of three-dimensional electron density of the following cell constants are given: $(C_iH_i)(CO_i) = (C_iH_i)I$ $a = b(\lambda) = 2.39 \pm 0.04 = 2.01 \pm 0.02 = 6.08$ $c(\lambda) = 8.54 \pm 0.03 = 8.22 \pm 0.02$ $c(\lambda) = 6.08 = 6.08$ $d_{measure}(g(cm)) = 1.46 = 1.80$	AUTHORS:	Kitaygorodskiy, A. I., Strochkov, Yu. T., Khota ( T. L., Vol'pin, M. Ye., Kursanov, D. M.
ABSTRACT: X-ray diffraction study of the structure of trouding perchlorate and todide monocrystals was made, unitate method of three-dimensional electron density.  The following cell constants are given:	TITLE:	Crystal Structure of Tropylium Perchlorate and tollar
perchlorate and iodide monocrystals was made, the method of three-dimensional electron density.  The following cell constants are given:	PERIODICAL:	Tzvestiya Akademii nauk SSSR. Otdeleniye biili banan nauk, 1960, Nr 1, pp 39-44 (USSR)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ABSTRACT:	the method of three-dimensional electron density contains.  The following cell constants are given:
	Card 1/5	(A) 8.54±0.04 8.22+0.04 $V(A^0)$ 652 678 A (a(sr <sup>2</sup> ) ~1.4 ~1.8

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2"

### "APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2

Crystal Structure of Tropylium Perchlorate and Iodide

78061 **S07/**62-60-1-7/70

The radius of tropylium ring, length of C = 0 long and other data are given in Figs. 1, 2, 3, 4, and 5. There are 5 figures; and 5 references, 1 U.K... Danish, 3 Soviet. The U.K. reference is: M. G. S. Dewar, R. Pettit, J. Chem. Soc., 20 1 (1956).

ASSOCIATION:

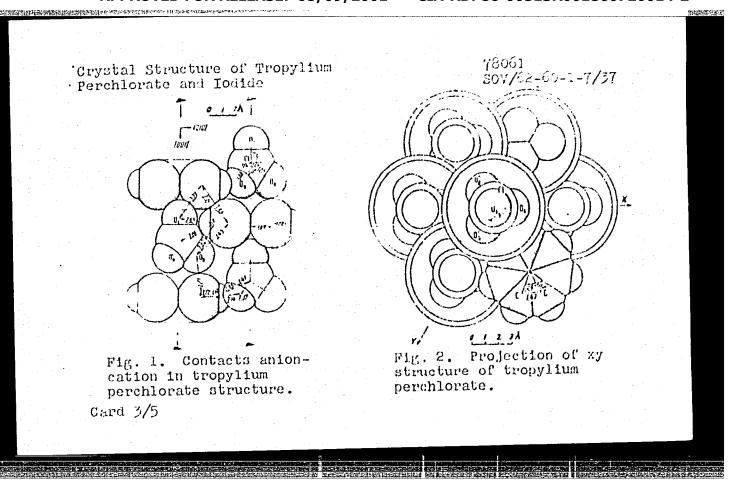
Institute of Element-Organic Compounds Academy of Sciences USSR (Institut elementoorganicheskikh

soyedineniy Akademii nauk SSSR)

SUBMITTED:

April 30, 1958

Card 2/5



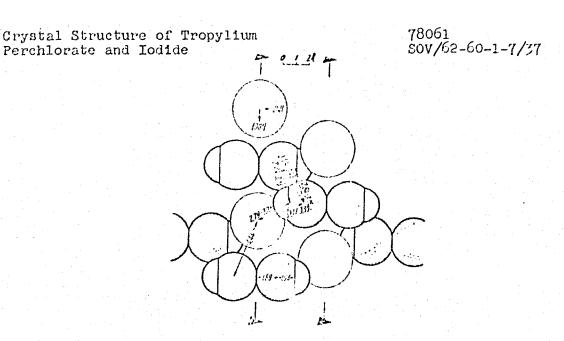


Fig. 3. Ions packing in structure of tropylium iodide.

c rd 4/5

Crystal Structure of Tropylium Perchlorate and Iodide

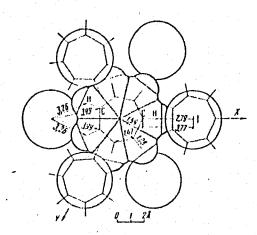
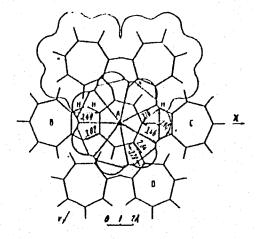


Fig. 4. Contacts cation-anion Fig. 5. Contacts cation-cation in structure of tropylium iodide. in structure of tropylium iodide.

78061 sov/62-60-1-7/37



Card 5/5

VOL'PIN, M.Ye.; PARNES, Z.N.; KURSANOV, D.N.

Hydride transfer in ditroppl ether, resulting in the formation of tropone and tropplidene. Izv.AN SSSR Otd.khim.nauk no.5:950 My \*60. (MIRA 13:6)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR. (Cycloheptatrienone) (Tropylium compounds) (Tropylidene)

5.3700

2209, 1308, 1153

S/062/60/000/010/017/018

B015/B064

AUTHORS:

Vol'pin, M. Ye., and Kursanov, D. N.

TITLE:

The Germanium Analog of Carbenes

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh

nauk, 1960, No. 10, p. 1903

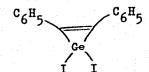
TEXT: In a previous paper (Ref.1), the authors jointly with Yu. D. Koreshkov investigated compounds of divalent carbon. Proceeding from the fact that an analogy exists between the electron structure of the derivatives of divalent germanium and divalent carbon, the authors studied the reaction between Ge<sup>2+</sup> and substances with multiple carbon-carbon bonds, i.e., tolanes. By heating GeI<sub>2</sub> with tolane, a stable addition product relating point at 300 5 3020C was obtained the gross

dition product, melting point at 300.5-303°C, was obtained, the gross formula is given as C14H10GeI2. The most probable structural formula is

Card 1/2

The Germanium Analog of Carbenes

s/062/60/000/010/017/018 B015/B064



This substance is soluble in benzene, carbon tetrachloride, and alcohol, and insoluble in ether, heptane, and water. With silver nitrate in an alcoholic solution, silver iodide rapidly precipitates. Thus, it may be assumed that the addition of GeI<sub>2</sub> to the triple bond of tolane proceeds analogously to the addition of carbene dihalides. There is 1 Soviet reference.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii

nauk SSSR (Institute of Elemental-organic Compounds of

the Academy of Sciences USSR)

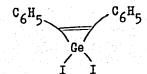
SUBMITTED:

July 19, 1960

Card 2/2

The Germanium Analog of Carbenes

S/062/60/000/010/017/018 B015/B064



This substance is soluble in benzene, carbon tetrachloride, and alcohol, and insoluble in ether, heptane, and water. With silver nitrate in an alcoholic solution, silver iodide rapidly precipitates. Thus, it may be assumed that the addition of GeI, to the triple bond of tolane proceeds analogously to the addition of carbene dihalides. There is ! Soviet reference.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii

nauk SSSR (Institute of Elemental-organic Compounds of

the Academy of Sciences USSR)

SUBMITTED:

July 19, 1960

Card 2/2

AUTHOR:

Vol'pin, M.Ye.

\$/074/60/029/03/002/004

B008/B006

TITLE:

Monbenzenoid Aromatic Compounds and the Concept "Aromatic"

PERIODICAL: Uspekhi khimii, 1960, Vol 29, Nr 3, pp 298-363 (USSR)

ABSTRACT:

The author gives a survey of the development of the chemistry of aromatic compounds. The characteristic properties and the structure of various nonbenzenoid, mainly carbocyclic, aromatic compounds are discussed here in greater detail. The term "aromatic" was coined nearly a hundred years ago, and was at first solely a description of quality without any physical meaning. Today, most of the numerous hypotheses on the structure of benzene and polynuclear aromatic compounds formed around the turn of the century are only of historic interest (Refs 4-19). The development of quantum-mechanical concepts of the nature of the chemical bond and the results obtained in the field of organic synthesis changed the ideas of the concept of aromatic compounds and their peculiarities, and considerably increased the number of systems which could be termed "aromatic". It was found that organic anions, organic cations, bipolar compounds, organometallic compounds, and several inorganic compounds, the composition and properties of which deviate completely from those of the traditional aromatic benzene derivatives, can be classed to the group of aromatic compounds. In this development, the method of

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APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2" Monbensenoid Aromatic Compounds and the Concept "Aromatic"

S/074/60/029/03/002/004 B008/B006

molecular orbits, first applied by Hückel (Refs 20,21), is of particular significance. Of the two chief calculation methods of quantum chemistry - the valence bond method and the method of molecular orbits - only the latter gives a correct picture of aromatic behavior. By this method it was possible to define the main criteria of the aromatic state. The author supplements and gives a more exact formulation of the definition of aromatic compounds by Dewar (Ref 331), which is repeatedly referred to lately: "Unsaturated cyclic compounds are aromatic, if all the atoms of the ring take part in the formation of a uniform conjugate system in which the x-electrons form a closed electron sheath". By the latter expression, one understands a  $\pi$ -electron system in which both the removal and the addition of electrons increase the total energy of the system and thus reduce its stability. Speaking in terms of the theory of molecular orbits this means that all the x-electrons are placed in bonding molecular orbits, two electrons being in each of them. The formation of a closed electron sheath is the cause of the physical and chemical properties characteristic of all aromatic systems: high stability, comparatively easy formation, the occurrence of substitution rather than addition to multiple bonds, bond lengths intermediate between single and double bonds, a planar or practically planar molecule,

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Monbengenoid Aromatic Compounds and the Concept "Aromatic"

S/074/60/029/03/002/004 B008/B006

equality of carbon-carbon bonds in unsubstituted monocyclic carbon rings. Great success in the field of synthesis and investigation of nonbenzenoid aromatic systems was achieved in the last decade. In this new field of organic chemistry a close contact between quantummechanical and synthetic methods is observable, which rendered it possible to predict a series of novel aromatic systems. In the present paper the author discusses the following aromatic compounds: the cyclopentadienide anion (the suffix "ide" is widely used to designate organic anions at present) (Refs 22, 40-88), tropylium cation (Refs 26, 89-140), cyclopropenylium cation (Refs 22, 141-145), azulenes (Refs 146-174), cyclobutadiene (Refs 175-222), cyclocotatetraene 7 (Refs 25, 27, 223-231), pentalene and heptalene (Refs 19, 25, 232-263), polycyclic systems (Refs 23, 264-275), macrocyclic aromatic systems table p 344 - (Refs 238, 276 - 288), aromatic metal complex compounds 7 (Refs 289-301), aromatic heterocyclic compounds (Refs 2,20,73,268, 302-307), inorganic aromatic compounds (Refs 308-330). The concept of the specific stability of the 6-electron system was successfully applied by Syrkin (Ref 332) to interpret a large number of organic reactions. In the next years, a rapid development of the chemistry of aromatic nonbenzenoid compounds is to be expected, especially the synthesis of new aromatic macrocyclic compounds, the cyclopropenylium

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Monbenzenoid Aromatic Compounds and the Concept "Aromatic"

B/074/60/029/03/002/004 B000/B006

cation as well as of new heterocyclic, polycyclic, and inorganic systems. The application of aromatic nonbenzenoid compounds opens up new ways of obtaining various substances with hitherto unattainable properties. The following persons are mentioned:

D.N. Kursanov, Z.N. Parnes, N.K. Baranetskaya, V.N. Setkina, A.A.

Balandin, M.L. Khidekel', V.G. Dulova, A.I. Kitaygorodskiy, I.S.

Akhrem, D.A. Bochvar, I.V. Stankevich, A.L. Chistyakov, Yu.D. Koreshkov, A.Ye. Favorskiy, T.A. Favorskaya, I.L. Knunyants, B.L. Dyatkin, N.P. Gambaryan, M.Ye. Dyatkina, Ye.M. Shustorovich, Yu.A. Zhdanov, A.N. Nesmeyanov, E.G. Perevalova, Ya.K. Syrkin, and the author of the present paper, A.M. Butlerov, Shidlovskaya. There are 1 table and 333 references, 49 of which are Soviet.

ASSOCIATION: In-t elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds of the AS USSR)

Card 4/4

S/079/60/030/04/28/080 B001/B016

AUTHORS:

Vol'pin, M. Ye., Akhrem, I. S., Kursanov, D. N.

TITLE:

Reaction of Tropylium Salts With Compounds Having a

Mobile Hydrogen

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 4, pp. 1187-1190

TEXT: In continuation of their previous papers (Refs. 1, 2), the authors investigated in the present paper the reaction of tropylium bromide with derivatives of carboxylic acids and with ketones. The aliphatic monocarboxylic acids (acetic, propionic, and butyric acid) and their esters (methyl-, ethyl acetate, ethyl propionate) were found not to react with tropylium salts even on prolonged heating. It is different with compounds in which the mobility of the  $\alpha$ -hydrogen atoms is increased by introducing activating substituents. Malonic acid, acetoacetic ester, cyanoacetic ester, and nitro-acetic ester react immediately with the above salts, already at room temperature. In all cases, the corresponding substitution products are obtained, with the cycloheptatrienyl radical being substituted for one hydrogen atom (Scheme 1). Ketones with a

Card 1/3

Reaction of Tropylium Salts With Compounds Having a Mobile Hydrogen

S/079/60/030/04/28/080 B001/B016

carbonyl group without activating substituents (acetone, acetophenone) enter into reaction with tropylium under far more rigorous conditions. On prolonged heating of the ketones with tropylium bromide, the substitution of the α-hydrogen atom takes place under formation of a monosubstituted product (Scheme 2). The introduction of a second carbonyl group considerably activates the molecule. Thus, acetyl acetone reacts immediately with tropylium salts, already in the cold. When treating tropylium bromide dissolved in water, the dicycloheptatrienyl ester is known to be formed (Ref. 3). The C-O bond in this compound, contrary to the common ethers, is very unstable, and readily breaks when treated with mineral acids to give tropylium salts:

Card 2/3

8/079/60/030/04/28/080 B001/B016

Reaction of Tropylium Salts With Compounds Having a Mobile Hydrogen

ASSOCIATION: Moskovskiy institut elementoorganicheskikh soyedineniy (Moscow Institute of Elemental-organic Compounds)

April 27, 1959 SUBMITTED:

Card 3/3

APPROVED FOR RELEASE: 08/09/2001 CIA-RDP86-00513R001860720014-2" KURSAHOV, D.N.; VOL'PIN, M.Ye.; KORESHKOV, Yu.D.

Interaction of dihalo carbenes with tolan. Synthesis of diphenylcy-clopropenone and of diphenylhydroxycyclopropenylium salts. Zhur. ob. khim. 30 no.9:2877-2884 S 160. (MIRA 13:9)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR. (Cyclopropenone)

VOL'PIN, M.Ye.; KORESHKOV, Yu.D.; KURSANOV, D.N.
Silicon analog of carbenes and the synthesis of a silicon-

Silicon analog of carbenes and the synthesis of a silicon analog of carbenes and the synthesis o

1. Institut elementoorganicheskikh soyedineniy AN SSSR. (Silicon organic compounds)

ZAYTSEV, B. Ye.; KORESHKOV, Yu.D.; VOL'PIN, M.Ye.; SHEYMKER, Yu.N.

Structure of diphenylcyclopropenone and tropone salts. Dokl. AN SSSR 139 no.5:1107-1109 Ag 161. (MIRA 14:8)

1. Institut khimii prirodnykh soyedineniy AN SSSR i Institut elementoorganicheskikh soyedineniy AN SSSR. Predstavleno akademikom M.M. Shemyakinym.

(Propenone) (Cycloheptatrienone)

KURSANOV, D.N.; VOL'PIN, M.Ye., doktor khimicheskikh nauk

New nonbenzenoid aromatic systems and the problem of aromaticity.

Zhur. VKHO 7 no.3:282-290 162.

1. Chlen-korrespondent Akademii nauk SSSR (for Kursanov).

(Aromatic compounds)

VOL'PIN, M.Ye.; KURSANOV, D.N.

Three-membered aromatic heterocycles. Part 1: Theoretical premises. Zhur.ob.khim. 32 no.4:1137-1141 Ap '62. (MIRA 15:4)

1. Institut elementoorganicheskikh soyedineniy.
(Heterocyclic compounds)

VOL'PIN, M.Ye.; KURSAMOV, D.N.

Three-membered aromatic heterocycles. Part 2: Preparation. Carbenes and carbenoids. Zhur.ob.khim. 32 no.4:1142-1146 Ap '62. (MIRA 15:4)

1. Institut elementoorganicheskikh soyedineniy. (Garbenes) (Heterocyclic compounds)

VOL'PIN, M.Ye.; KURSANOV, D.M.

Three-membered aromatic heterocycles. Part 3: Reaction of a germanium analog of carbenes with tolan. Synthesis of a germanium-containing three-membered ring. Zhur.ob.khim. 32 no.5:1455-1460 My 162. (MIRA 15:5)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

(Germanium organic compounds) (Heterocyclic compounds)

VOL'PIN, M.Ye.; SHUR, V.B.

Nitrogen fixation on complex catalysts. Dokl. AN SECR 156 1102-1104 Je 164. (MIRA 17:6)

1. Institut elementoorganicheskikh soyedineniy AN SSSR. Predstavleno akademikom A.N.Nesmeyanovym.

L 05165 ACC NR: A	.67 EWI(m)/EWP(j) RM SOURCE CODE: UR/0062	/66/000/006/1083/108	4
Compound	M. Ye., CHAPOVSKAYA, N. K., SHUR, V. B., Institute of Academy of Sciences USSR (Institut elementoorganiche	skiki solednem	
AN SSSR) "Reaction Metals"  (	of Nitrogen with Systems Based on Phosphine Complexes	of Transition 3	
Moscow, 1 pp 1083-1	zvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No .084	6, 1966,	
Abstract	The reaction of nitrogen with systems produced by the phosphine complexes of transition metals [(Ph <sub>3</sub> P) <sub>2</sub> TiCl <sub>2</sub> , (Ph <sub>3</sub> P) <sub>2</sub> NiCl <sub>2</sub> , (Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub> , and (Ph <sub>3</sub> P) <sub>2</sub> PtCl <sub>2</sub> ] with	ne reaction of a	
(Ph <sub>3</sub> P) <sub>2</sub> Co	Cl <sub>2</sub> , (Ph <sub>3</sub> P) <sub>2</sub> NiCl <sub>2</sub> , (Ph <sub>3</sub> P) <sub>2</sub> PdCl <sub>2</sub> , and (Ph <sub>3</sub> P) <sub>2</sub> PtCl <sub>2</sub> ] with a [C <sub>2</sub> H <sub>5</sub> MgBr in ether, n-C <sub>4</sub> H <sub>5</sub> Li in n-heptane, and (i-C <sub>4</sub> H <sub>5</sub> Li)	h organometallic  (a) Al in n-heptane	
was stud	led. Systems including triphenylphosphine complexes of	Ti (IV) and re other systems	
studied,	as well as systems of the triphenylphosphine complexes	lve in the reac-	
acetylac	n nitrogen. The pattern observed was the same as for contents: the most active are compounds of the transition left-hand portion of the transition period. [JPRS: organometallic compound, organic phosphorus compounds.]	37.0237	
hydride	O7 who SUBM DATE: 05Nov65 / ORIG REF: 004 44 OT		

ACC NR: AP7011354

SOURCE CODE: UR/0062/66/000/011/2041/2042

0931 1733

AUTHOR: Vol'pin, M. Ye.; Kolomnikov, I. S.

ORG: Institute of Heteroorganic Compounds, Academy of Sciences USSR (Institut elementoorganicheskikh soyedineniy AN SSSR)

TITLE: Complex of zero-valent cobalt with triethylphosphite

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 11, 1966, 2041-2042

TOPIC TAGS: cobalt compound, phosphate ester, electron paramagnetic resonance

SUB CODE: 07

ABSTRACT: In an earlier report, the production of phosphite complexes of univalent cobalt L4CoCl and L3CoCl, where L = (C2H5O)3P, was announced. Under homogeneous conditions, these complexes were found to absorb molecular hydrogen, yielding a complex of zero-valent cobalt, with the composition L4Co -- the first representative of complexes of zero-valent cobalt with phosphorus ligands. This complex was found to be a white crystalline substance, stable in air for several hours. Electron paramagnetic resonance studies indicated that the complex exists in dimer form. The absence of a Co-H bond was demonstrated by a study of the infrared spectrum and by reactions with iodine and carbon tetrachloride. The authors thank v. I. Belovaya, Cord 1/2

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ACC NR: AP7011354

of the Institute of Inorganic Chemistry, AN SSSR, for measuring the magnetic susceptibility, and V. I. Sheychenko, of the Institute of Natural Compounds, AN SSSR, for taking the spectrums of the YaMR. Orig. art. has: 1 formula. [JPRS: 40,351]

Card 2/2

YOL'PIN, M.Ye.; ILATOVSKAYA, M.A.; LARIKOV, Ye.I.; KHIDEKEL', M.L.; SHVETSOV, Yu.A.; SHUR, V.B.

Nitrogen fixation on hydrogen-activating transition metal complexes. Dokl. AN SSSR 164 no.2:331-333 S '65.

(MIRA 18:9)

1. Institut elementoorganicheskikh soyedineniy AN SSSR i Institut khimicheskoy fiziki AN SSSR. Submitted February 15, 1965.

VOL'PIN, M.Ye.; SHUR, V.B.; BICHIN, L.P.

Study of nitrogen fixation on complex catalysts by means of H<sup>15</sup>.

Izv. AN SSSR. Ser. khim. no.4:720-721 '65. (MIRA 18:5)

1. Institut elementoorganicheskikh soyedineniy AN SSSR i Institut biologicheskoy i meditsinskoy khimii AMN SSSR.

VOLIPIN, M.Ye.; AKHREM, I.S.

Light heterolytic rupture of the carbon-carbon bond in cycloheptatriene derivatives. Dokl. AN SSSR 161 no.3:597-600 Mr '65. ('TRA 18:4)

1. Institut elementoorganicheskikh soyedineniy AN SSSR. Submitted September 12, 1964.

VOL'FIN, M.Ye.; SHUR, V.B.; ILATOVSKAYA, M.A.

Fixation of nitrogen by the system based on dicyclopentadienyltitanium dichloride. zv.AN SSSR.Ser.khim. no.9:1728-1729 S 164. (MIRA 17:10)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

TERENT'YEV, Aleksendr Fetrovich; POTAPOV, Viktor Mikhaylovich; KOLOSOV, M.N., st. nauchn. sotr., retsenzent; VOL'PIN, M.Ye., doktor khim. nauk, red.

[Principles of stereochemistry] Osnovy stereokhimii. Moskva, Khimiia, 1964. 687 p. (MIRA 17:12)

VOL'PIN, M.Ye.; STRUCHKOV, Yu.T.; VILKOV, L.V.; MASTRYUKOV, V.S.; DULOVA, V.G.; KURSANOV, D.N.

Structure of the products obtained in the reaction of acetylene with bivalent derivatives of germanium. Izv. AN SSSR. Ser. khim. no.11:2067 N '63. (MIRA 17:1)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

VOL'PIN, M.Ye.; DUBOVITSKIY, V.A.; NOGINA, O.V.; KURSANOV, D.N.

Titanocene compound with tolan. Dokl. AN SSSR 151 no.5:1100-1103
Ag '63. (MIRA 16:9)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
2. Chlen-korrespondent AN SSSR (for Kursanov).

(Titanium) (Acetylene)

LETTES, L.A.; DULOVA, V.G.; VOL'PIN, M.Ye.

Three-membered aromatic heterocycles. Report No.5: Vibrational spectra and structure of germanium heterocycles. Izv. AN SSSR. Otd.khim. nauk no.4:731-737 Ap 163. (MIRA 16:3)

1. Institut elementoorganicheskikh soyedineniy AN SSSR i Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR. (Germanium organic compounds—Spectra) (Heterocyclic compounds)

VOL'PIN, M.Ye.; DULOVA, V.G.; KURSANOV, D.N.

Three-membered aromatic heterocycles. Report No.4: Reaction of germenium diiodide with acetylene and the synthesis of a three-membered heterocycle and germanium-containing polymer. Izv. AN SSSR. Otd.khim. nauk no.4:27-731 Ap 163. (MIRA 16:3)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.

(Germanium organic compounds) (Heterocyclic compounds)

EYDUS, Ya.T.; NEFEDOV, B.K.; VOL'PIN, M.Ye.

Formation of cycloheptatriene from benzene, carbon monoxide, and hydrogen on cobalt catalysts. Izv.AN SSSR.Otd.khim.nauk no.3:548-552 Mr 163. (MIRA 16:4)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR i Institut elementoorganicheskikh soyedineniy AN SSSR. (Cycloheptatriene)

"Concerning the Weight of Bicompacts." Thesis for degree of Cand. Physicomathematical Sci. Sub. 1 Jun 49, Sci Res Inst of Mathematics, Moscow Order of Lenin State U imeni M. V. Lomonosov.

Summary 82, 18 Dec 52, <u>Dissertations Presented For Degrees in Science and Engineering in Moscow in 1949</u>. From <u>Vecherovaya Moskva</u>. Jan-Dec 1949.

VOL'PIN, A.S.

CAND PHYSICOMATH SCI.

Dissertation: "Concerning the Weight of Bicompacts."

1 June 49
Sci Res Inst of Mathematics, Moscow Order of Lenin State V imeni M.V. Lomonosov.

SO Vecheryaya Moskva Sum 71

VOL'PIN, E.I.

Sanitariia i gigiena v miasnoi i molochnoi promyshlennosti [Sanitation and hygiene in the meat and milk industry]. Moskva, Pishchepromizdat, 1953. 121 p.

SO: Monthly List of Russian Accessions, Vol. 6, No. 2, May 1953